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Supersonic Jet Studies of Fluorene Clustered with Water, Ammonia
and Piperidine

by

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AMMONIA AND PIPERIDINE

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Abstract

Mass resolved excitation spectroscopy and dispersed emission spectroscopy are employed to study van der Waals (vdW) clusters of jet cooled fluorene with ammonia, water and piperidine. For fluorene(H₂O)₁ and fluorene(NH₃)₁ clusters, cluster geometries and binding energies can be suggested based on the experimental results and Lennard-Jones (LJ) potential (6-12-1) energy calculations. As the number of solvent molecules in the cluster is increased, spectra of the clusters become more complex and broad probably due to the many possible stable configurations for these vdW clusters. Although the pK_a for fluorene in its first excited singlet state (Förster cycle calculations) is quite acidic (-8.6), and solvent molecules can coordinate to the aliphatic hydrogens of the fluorene molecule in at least some cluster configurations, no direct evidence is found for the occurrence of proton transfer in S₁ in these systems.

I. Introduction

The acidities of aromatic hydrocarbons in their first excited singlet states can be predicted by using Förster cycle calculations.¹ Based on this calculation, the pK_a of fluorene in the first excited singlet state S_1 has been estimated to be -8.6, whereas it is measured to be 20.5 in the ground state, S_0 .² Because of this large electronic redistribution upon electronic excitation in fluorene, very different acid-base properties, dipole moment and solvent organization can be expected for the ground and first excited singlet states. The aliphatic protons in fluorene might then become labile in S_1 , making fluorene a good candidate for the study of intermolecular proton transfer dynamics.

Recent gas phase studies have demonstrated that solvent mediated intermolecular proton transfer reactions can be investigated using supersonic molecular jet spectroscopy. These reactions are confirmed by observing broad and red shifted fluorescence originating from the S_1 state of the anion formed by proton transfer. The minimum number of solvent molecules N_c required for proton transfer has also been determined in these studies.

In the proton transfer reaction of α -naphthol with ammonia, N_c has been determined to be 4.³⁻⁵ In a related set of experiments on ions, Solgadi et al. have proposed that proton transfer may occur in phenol/ammonia complexes when the number of ammonia molecules exceeds 4.⁶ Nimlos et al. have determined that proton transfer occurs in 2-hydroxypyridine/ammonia clusters for $n \geq 3$.⁷

These studies demonstrate that in vdW clusters a number of solvent molecules must be present to induce proton transfer: some

minimum degree of solvation of the proton and/or anion by solvent molecules is necessary for proton transfer to occur.

Supersonic jet techniques are typically employed for generating and studying the various requisite vdW clusters.⁸ vdW clusters of fluorene with water, ammonia and piperidine are produced in the supersonic jet expansion and are then identified and investigated by mass resolved excitation spectroscopy (time-of-flight mass spectroscopy-TOFMS) and dispersed emission (DE).

In this report, we present and analyze mass resolved excitation data, DE data and the results of potential energy calculations for fluorene complexed with water, ammonia and piperidine. The calculations help in the determination of the cluster configuration, binding energies and the expected cluster spectroscopic shifts. We have found them quite helpful in the overall determination of the behavior of these clusters.⁹ The possibility of an intermolecular proton transfer reaction in fluorene complexes will be discussed based on the experimental observations and calculations.

II. Experimental Procedure

The supersonic jet apparatus has been described in detail previously.¹⁰ For time-of-flight mass spectroscopy, the doubled output of two pulsed dye lasers, each of which is pumped by the doubled output of a Nd:YAG laser, is used to excite the fluorene molecule and cluster to S_1 , and then ionize it. The pump laser ($S_1 \leftarrow S_0$ excitation) is scanned while the ionization laser (ion $\leftarrow S_1$ excitation) is held at a fixed frequency. The energy of the ionization laser is kept lower than that of the pump

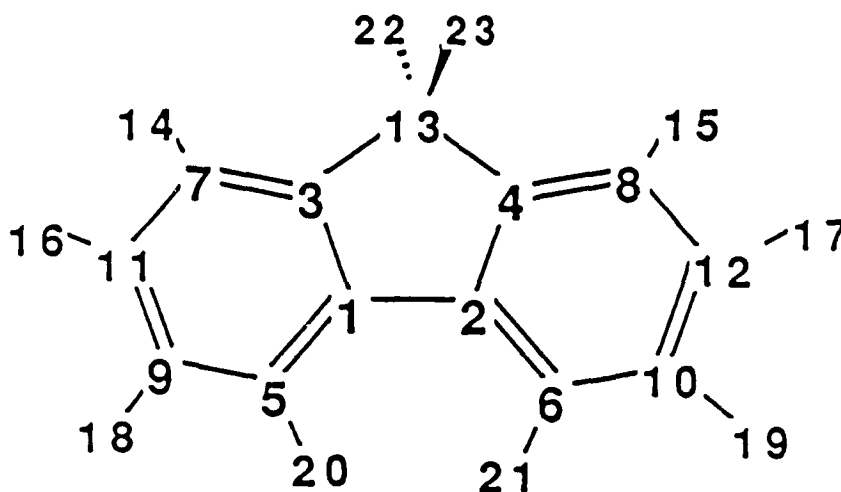
laser so as to minimize the fragmentation of the clusters. The two laser beams are made collinear and intersect the expansion gas at right angles. The ions produced are accelerated up the flight tube and detected by a microchannel plate. For the dispersed emission (DE) ~~detection~~ system¹¹ a 1 m McPherson monochromator with a 1200 g/mm grating is used in the third order to resolve the fluorescence. The emitted light is detected by a photomultiplier tube.

Supersonic expansions are created in a vacuum chamber using a pulsed nozzle with a 0.7 mm diameter orifice, or a cw nozzle with a 0.1 mm diameter orifice. Samples of fluorene are placed in the head of the nozzle, enabling the samples to be heated to 70°C in the pulsed nozzle, and 150°C in the cw nozzle.

The expansion gas is typically helium and the backing pressure is about 3 to 4 atm. Mixtures of helium with NH₃, ND₃, H₂O, D₂O and piperidine are prepared before they enter the nozzle. The concentration of each solvent is monitored to be 1 or 1.5% in He. Fluorene is purchased from Aldrich and used without additional purification.

The stable geometries of various clusters are calculated using empirical atom-atom potential energy calculations developed by Scheraga et al.¹² The potential function form is described in detail in a previous publication.⁷ The partial charges for each molecule are calculated from the MOPAC (v. 5.0) programs.¹³ Table I contains the partial charges of the solute molecule (fluorene), and in Table II the partial charges of the solvent molecules are presented. The atomic numbering of the fluorene molecule is shown in Scheme I.

Scheme I.



III. Results and Discussion

A. Isolated fluorene molecule.

The fluorescence excitation and TOFMS of jet cooled fluorene have been reported previously.¹⁴ The TOFMS of fluorene ($m/e = 166$) is shown in Figure 1 and is similar to that reported by Leutwyler et al.^{14(b)} The origin is identified at 33778.1 cm^{-1} . The other two intense peaks in the spectrum at $+208$ and $+408 \text{ cm}^{-1}$ from the spectral origin are assigned as the totally symmetric 1^1 and 2^1 vibrational modes of S_1 , respectively. The assignments are based on those given in reference 14(b).

The DE spectrum of jet cooled isolated fluorene, excited at the origin (33778.1 cm^{-1}), is shown in Figure 2. The two vibrational modes 1_1 and 2_1 in the ground state are identified at 210 and 411 cm^{-1} , respectively.

B. Fluorene/water clusters.

Figure 3 shows the TOFMS of fluorene(H_2O)₁ as a function of ionization energy. As ionization energy is decreased, the intensity of two peaks, positioned at 33834.8 (I) and 33840.0 cm^{-1} (II), remains strong. Such an intensity dependence on the ionization energy in the fluorene(H_2O)₁ mass channel demonstrates that many of the features attributed to fluorene(H_2O)₁ are actually due to fragmentation of larger clusters (mostly the (H_2O)₂ cluster), caused by excess vibrational energy in the cluster ion. With the exception of the intense feature at 33840.0 cm^{-1} all the coincident features in the observed (H_2O)₁ and (H_2O)₂ cluster spectra are probably due to fragmentation of the fluorene(H_2O)₂ cluster. Although this latter peak is coincident in energy with a feature in the (H_2O)₂ cluster spectrum, its intensity behavior with ionization energy is not indicative of fragmentation of larger clusters.

The DE spectra of the fluorene(H_2O)₁ cluster excited at 33834.8 (I) and 33840.0 cm^{-1} (II) and the fluorene(H_2O)₂ cluster excited at 33821.3 cm^{-1} (III) are presented in Figure 4. The DE spectrum of fluorene(H_2O)₁ excited at 33834.8 cm^{-1} (I) (Figure 4a) evidences two strong peaks in the origin region with a spacing of 51.6 cm^{-1} . Figure 4c presents the DE spectrum of fluorene(H_2O)₂ excited at 33821.3 cm^{-1} (III), which shows a vibrational progression with the spacing of 32.4 cm^{-1} . Figure 4b shows three strong peaks in the origin region. The spacing between the origin peak and the next peak in this spectrum (Figure 4b) is exactly the same as that in the DE spectrum of fluorene(H_2O)₂ (32.4 cm^{-1} , Figure 4c) and that between the origin peak and the second peak is exactly the same as that in the DE of fluorene(H_2O)₁ (51.6 cm^{-1} , Figure 4a).

The above DE behavior supports the following conclusions: the peak at 33834.8 cm^{-1} (I) is only generated by the fluorene(H_2O)₁ cluster; the peak at 33840.0 cm^{-1} (II) is generated by both the fluorene(H_2O)_{1,2} clusters; the second peak (II) in the TOFMS of fluorene(H_2O)₁ is due to a vdW vibrational mode since the DE spectra excited at both positions I and II (Figure 3) evidence the same spacing; and only one origin (at 33834.8 cm^{-1}) is observed for fluorene(H_2O)₁.

Only one stable configuration of fluorene(H_2O)₁ (binding energy = 937 cm^{-1}) is obtained from LJ potential energy calculations. The structure of this minimum energy cluster is depicted in Figure 5. The oxygen atom of coordinated water is displaced from the center of mass of the fluorene molecule by 0.66 \AA along the X axis, and is 3.3 \AA above the fluorene ring. The water hydrogen atoms are 2.8 \AA above the ring.

The two color TOFMS of fluorene(H_2O)₂ clusters and the one color TOFMS of fluorene(D_2O)₁ cluster are presented in Figure 6. The TOFMS of fluorene(D_2O)₁ is taken with a high ionization energy (ca. 33800 cm^{-1}), so that both the mono- and di-solvate cluster spectra are present. The fluorene(H_2O)₂ cluster spectrum (Figure 6b) shows a progression in a low frequency mode with a spacing on the order of $\sim 11\text{ cm}^{-1}$. The spacing of this progression decreases to $\sim 6\text{ cm}^{-1}$ upon deuteration of the water molecule (See Table III). This isotope effect clearly demonstrates that the observed progression is associated with motion of the water molecule and the Franck-Condon intensity profile in this spectrum indicates that a large displacement of the water molecule occurs in the excited state relative to the ground state.

The isotope effect (11 cm^{-1} vs 6 cm^{-1}) for this vdW progression suggests that the motion of the active vdW mode could be a free rotation

of the water molecule about an axis that bisects the H-O-H angle because the moment of inertia for this rotation changes by a factor of two upon water deuteration. Nonetheless, the harmonic behavior of this vdW mode contradicts the free rotor explanation. At present, one can only conclude that the active vdW mode is related to the motion of hydrogen atoms most likely (but not definitely) on the water molecule.

The spectra for the mono- and di-hydrate fluorene complexes are blue shifted with respect to the isolated fluorene origin by ~ 57 and ~ 36 cm^{-1} , respectively. Cluster features for both the mono- and di-solvate complexes are also built on the 1^1 vibration 208 cm^{-1} to higher energy. The cluster features built on this vibration are identical to the cluster features built on the origin.

The spectra of fluorene(H_2O) $_n$ ($n=3$ to 5) are shown in Figure 7. The cluster spectra become increasingly broad as the number of water molecules increases. The position of the maximum spectral intensity (~ 34080 cm^{-1}) is almost unchanged as more waters are added to the fluorene(H_2O) $_n$ cluster: such behavior is typical of larger clusters.¹⁵ The increased broadening of the spectra with cluster size can be attributed to several factors: spectral congestion due to multiple cluster configurations, fragmentation of clusters, and/or proton transfer from fluorene to (H_2O) $_n$.

The DE spectra of fluorene(H_2O) $_n$ clusters ($n = 3$ to 5) excited at the common maximum intensity peak, 34080 cm^{-1} and at ~ 1000 cm^{-1} excess vibrational energy in S_1 look almost the same as those presented in Figure 4. No highly red shifted broad emission due to the excited fluorene anion (produced by proton transfer) is observed for this cluster system. Considering the basicity of water and its clusters,¹⁶ this is not a

surprising result. The broad and featureless spectra for large fluorene(H_2O) $_n$ clusters must then be attributed to the multiple configurations (and perhaps fragmentation) as n becomes large.

C Fluorene/ammonia clusters

The TOFMS of fluorene(NH_3) $_1$ ($m/e = 183$) is shown in Figure 8a. The spectrum is quite sharp and well resolved. The origin for the cluster is red shifted by 4 cm^{-1} with respect to that of the isolated molecule. Figure 8b depicts the TOFMS of fluorene(ND_3) $_1$ ($m/e = 186$). The first few features of the fluorene(NH_3) $_1$ and fluorene(ND_3) $_1$ spectra are nearly identical, showing little or no isotopic shift. One can conclude from this observation that at least the first few features correspond to clusters of different configurations.

LJ potential energy calculations support this expectation. Several different minimum energy conformers are obtained from the calculations; for example, one has a geometry in which the ammonia molecule above the fluorene molecule central ring and another has a geometry in which the ammonia molecule coordinates to the aliphatic hydrogens and is displaced from the fluorene ring (see Figure 9).

The TOFMS of fluorene(NH_3) $_2$ is shown in Figure 10a. The origin of this cluster appears as a doublet in the spectrum, red shifted by 51.3 cm^{-1} with respect to the origin of the isolated molecule. The spectrum of the fluorene(NH_3) $_2$ clusters becomes increasingly more complex at higher energy with several sharp features built on a broad background. The same pattern, both broad and sharp features, is seen to occur in the 1^1 spectral region ($\sim 208 \text{ cm}^{-1}$ above the origin). The width

of this broad peak is on the order of 100 cm^{-1} . The cause of the broadening for this relatively small cluster could be thought to be either dynamical processes or congestion from many possible cluster configurations.

The TOFMS fluorene(NH_3) $_n$ ($n = 3$ to 6) are also shown in Figure 10. The spectra are all similar: broad, diffuse and red shifted with respect to the isolated molecule. As in the TOFMS of larger fluorene/water clusters, the position of the maximum intensity peak does not change significantly with fluorene/ammonia cluster size for $n = 2$ to 6 . The position of this maximum intensity peak is $\sim 33810\text{ cm}^{-1}$.

DE spectra for fluorene(NH_3) $_1$ and fluorene(NH_3) $_2$, obtained by excitation at the cluster 0_0^0 , are presented in Figure 11. In both cases ($n = 1$ and 2), the spectra of the clusters are quite similar to that of the bare molecule with exception of the superimposed vdW cluster structure present in the cluster emission.

A careful search for anion emission (generated by proton transfer from larger fluorene(NH_3) $_n$ ($n \geq 3$) clusters was also performed with excitation energy at 33810 cm^{-1} . No additional broad fluorescence could be observed in the region $370\text{-}550\text{ nm}$. Moreover, dispersed emission spectra, taken with excess vibrational excitation energy in S_1 of nearly 1500 cm^{-1} , look identical to those presented in Figure 11. These observations suggest that the broadness of the fluorene(NH_3) $_n$ TOFMS is most probably caused by a variety of different cluster conformations for a given cluster mass and not proton transfer/fluorene anion generation.

D. Fluorene/piperidine clusters

The TOFMS of fluorene/piperidine clusters are present in Figure 12. The spectrum of the mono-solvate cluster (Figure 12a) is complex, consisting of both broad and sharp features. The first sharp feature observed in the fluorene(piperidine)₁ spectrum is assigned to be the origin of the spectrum. The cluster origin transition is red shifted by ~ 90 cm^{-1} compared to the bare fluorene molecule origin. The di-solvate spectrum is broad with little or no sharp features (Figure 12b).

DE spectra of piperidine complexes do not show direct evidence for an intermolecular proton transfer reaction: no broad, red shifted fluorescence is observed from this system.

E. Proton transfer reaction

Although a Förster cycle calculation of pK_a for the aliphatic hydrogen atoms of fluorene indicates that they should be very acidic ($\text{pK}_a = -8.6$) in the excited state and both calculations and experiments suggest that NH_3 and H_2O solvent molecules can coordinate to the aliphatic hydrogens of the fluorene molecule, none of the spectra of these vdW clusters gives any direct evidence for the occurrence of an intermolecular proton transfer reaction in S_1 (i.e., the generation of the fluorenyl anion). Excited state proton transfer can only be observed if the proton transfer occurs at least on the same time scale as the lifetime of the excited singlet state S_1 ($\tau(S_1) < 10$ ns). Förster cycle calculations also indicate a large change in pK_a for naphthalene upon excitation

($pK_a(S_0) = -4.0$, $pK_a(S_1) = 11.7$)^{17,18}; however, protonation of naphthalene does not occur upon singlet excitation. Protonation and deprotonation at carbon atoms is apparently quite slow compared to that at oxygen or nitrogen atoms^{19,20} and therefore may not be competitive with deactivation of the singlet excited state. Solution phase studies of proton transfer between the fluorene molecule and methoxy sodium show the rate of this reaction is $\sim 4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$; ¹⁹ proton transfer occurs in tens of microseconds. A large barrier to proton transfer must therefore exist for this excited state reaction.

IV. Conclusions

Fluorene(H_2O)₁, (NH_3)₁ vdW clusters show sharp mass resolved excitation spectra. As the number of solvent molecules is increased ($n \geq 2$) for these clusters, the TOFMS become more complex and broad due to spectral congestion from the many possible stable cluster configurations. In fluorene(H_2O)₁, only one cluster structure is observed with a (calculated) binding energy of 937 cm^{-1} . In fluorene(H_2O)₂, a significant displacement along the vdW coordinates occurs upon $S_1 \leftarrow S_0$ excitation. Studies of fluorene(NH_3)₁ and fluorene(ND_3)₁ suggest that at least two stable configurations of vdW clusters are possible in fluorene(NH_3)₁; one has a structure in which ammonia coordinates to the fluorene ring and the other has a structure in which ammonia is coordinates to the aliphatic hydrogens and is displaced from the fluorene ring.

Based on both calculations and interpretation of the fluorene/ammonia, water and piperidine cluster spectra, one expects that

the solvent molecules can coordinate to the aliphatic hydrogens of fluorene molecule in at least some cluster configurations. Nonetheless, no evidence (e.g., broad, red shifted fluorenyl anion emission) which substantiates an excited state intermolecular proton transfer reaction can be found in these systems. The absence of any observed anion emission suggests that the proton transfer reaction at the carbon center occurs at too slow a rate to be observed given the excited state lifetime of ca. 10 ns.

Acknowledgment

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Table I. Atomic partial charges for the fluorene molecule.

Atoms	Partial charges
C 1	-0.0407
2	-0.0407
3	-0.0773
4	-0.0773
5	-0.1039
6	-0.1039
7	-0.1184
8	-0.1184
9	-0.1328
10	-0.1328
11	-0.1258
12	-0.1258
13	-0.0879
H 14	0.1338
15	0.1338
16	0.1308
17	0.1308
18	0.1311
19	0.1311
20	0.1350
21	0.1350
22	0.1122
23	0.1122

- a. See Scheme 1 for detail
b. Geometry data are obtained from Ref. 21.

Table II. Partial atomic charges for water and ammonia molecules

Molecule	Atom	Partial Charge
H ₂ O	O	-0.3827
	H	0.1914
NH ₃	N	-0.3957
	H	0.1319

Table III. The observed vdW vibrational energy levels for S_1 of fluorene(H_2O)₂ and fluorene(D_2O)₂.

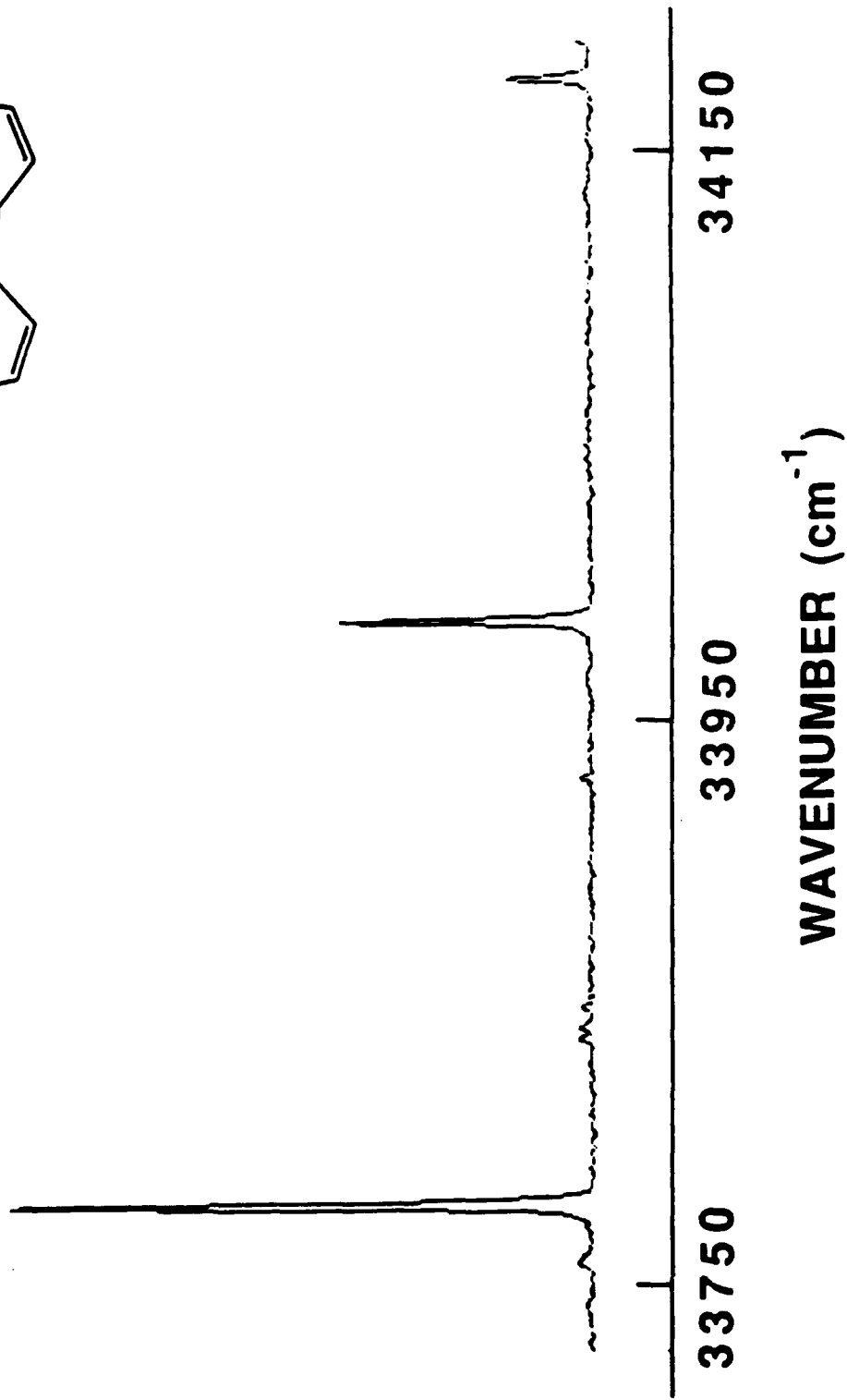
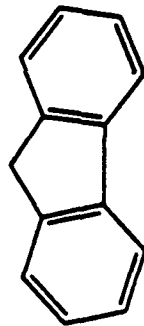
Fluorene(H_2O) ₂ (cm^{-1})	Fluorene(D_2O) ₂ (cm^{-1})
0(33821.3 cm^{-1})	0(33832.9 cm^{-1})
9.20	5.72
21.13	10.69
33.00	17.16
44.69	21.63
55.63	28.10
67.07	34.31
79.00	39.29
-	44.26
-	49.98
-	55.94
-	62.41

Figure Captions

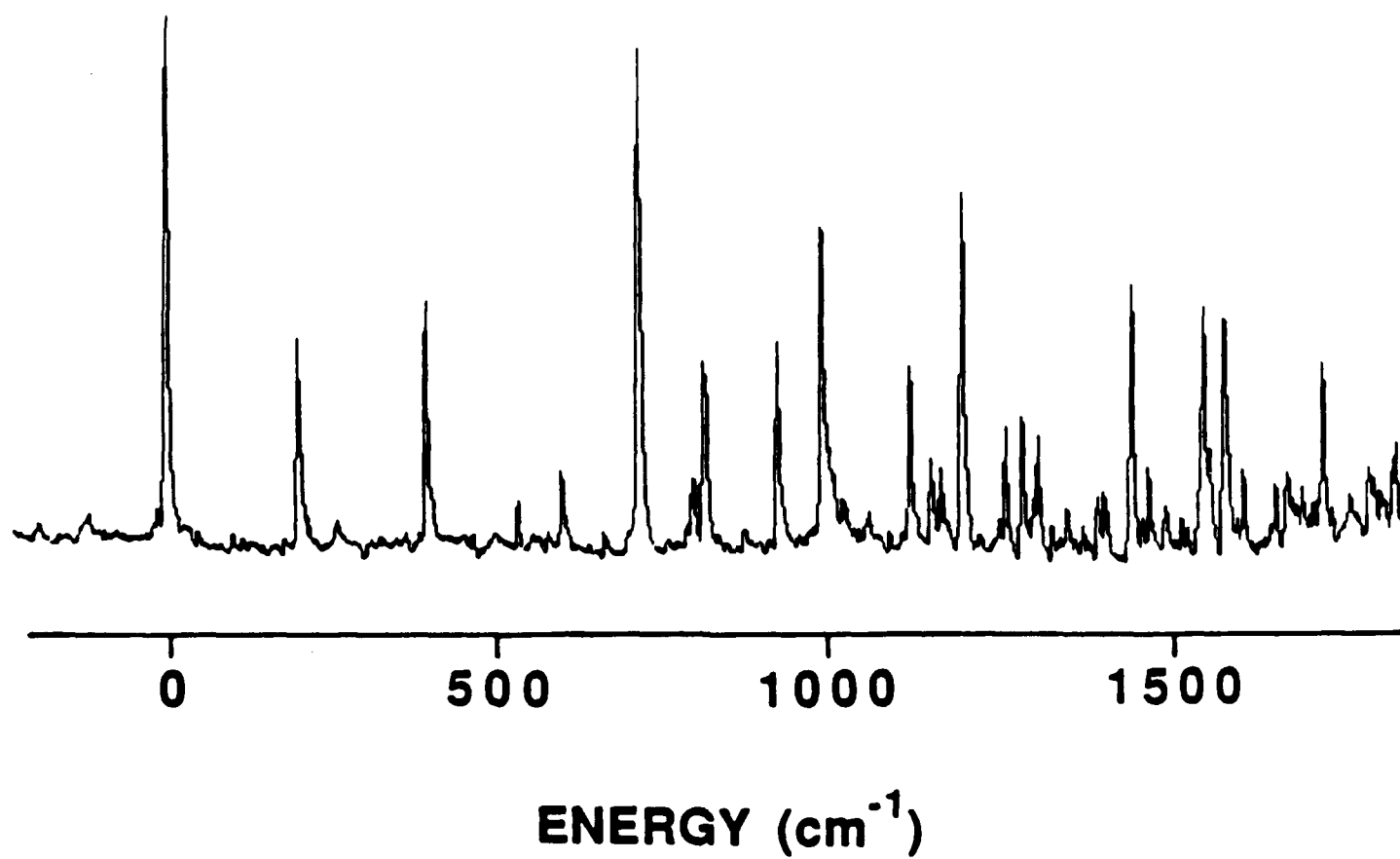
1. The two-color TOFMS of jet cooled fluorene. The origin, 0_0^0 transition, for the $S_1 \leftarrow S_0$ transition is at 33778.1 cm^{-1} . The two features $+208$ and $+408 \text{ cm}^{-1}$ from the origin are assigned to the totally symmetric vibrations ν_1 and ν_2 .
2. Dispersed emission spectrum of jet cooled fluorene. The excitation energy is 33778.1 cm^{-1} , corresponding to the origin transition.
3. TOFMS of fluorene(H_2O)₁ clusters as a function of ionization energy, E_{ion} . a. $E_{\text{ion}} = 33333.0 \text{ cm}^{-1}$ b. $E_{\text{ion}} = 31250.0 \text{ cm}^{-1}$ c. $E_{\text{ion}} = 30769.2 \text{ cm}^{-1}$
4. Dispersed emission spectra of fluorene(H_2O)_n, ($n = 1, 2$) clusters: a. excitation at $33,834.8 \text{ cm}^{-1}$, the feature marked I in Figure 3 - the transition pumped is assigned to the fluorene(H_2O)₁ cluster exclusively; b. excitation at $33,840.3 \text{ cm}^{-1}$, the feature marked II in Figure 3 - the transition pumped is assigned as coincident fluorene(H_2O)₁ and (H_2O)₂ cluster transitions; c. excitation at $33,821.3 \text{ cm}^{-1}$, the feature marked III in Figure 3 - the transition pumped is assigned exclusively to the fluorene(H_2O)₂ cluster.
5. Minimum energy configuration and binding energy for fluorene(H_2O)₁ obtained using a LJ potential calculation.
6. Fluorene/water cluster TOFMS are shown near the origin region for (H_2O)₁, (H_2O)₂ and (D_2O)₁. The TOFMS of fluorene(H_2O)₁ and fluorene(H_2O)₂ are very similar due to the fragmentation of the di-solvate into the mono-solvate mass channel (see text). The spacing in the vdW mode progression has decreased by approximately one-half in the fluorene(D_2O)₁ spectrum.
7. TOFMS of fluorene(H_2O)_n ($n = 3$ to 5). The spectra are all broad with sharp features built on the broad background. The negative peak at $33,982 \text{ cm}^{-1}$ is due to saturation of the microchannel plate from the ν_1 vibration of isolated fluorene.

8. TOFMS of the fluorene(ammonia)₁ cluster for both NH₃ and ND₃. The spectra consist of sharp features. In contrast to the results for water clusters, an isotope shift is not observed for the van der Waals modes upon deuteration of ammonia.
9. Minimum energy configurations and binding energies for fluorene(NH₃)₁ obtained using a LJ potential calculation.
10. TOFMS of fluorene(NH₃)_n, n = 2 to 4 and 6. The origin of the TOFMS of fluorene(NH₃)₂ (taken as the lowest energy doublet) is red shifted by 51 cm⁻¹ from that of the isolated molecule. The spectrum of the di-solvate is quite complex consisting of sharp features built on a broad background. As the number of ammonia molecules increases in the cluster, the number of sharp features in the spectrum diminishes and the spectrum becomes broad and featureless.
11. Dispersed emission spectra for fluorene(NH₃)₁ and fluorene(NH₃)₂. The origin was excited for each of these two clusters, at 33774.1 and 33728.6 cm⁻¹ for mono- and di-solvate, respectively.
12. TOFMS of fluorene(piperidine)_n clusters.
(a) (piperidine)₁ (b) (piperidine)₂

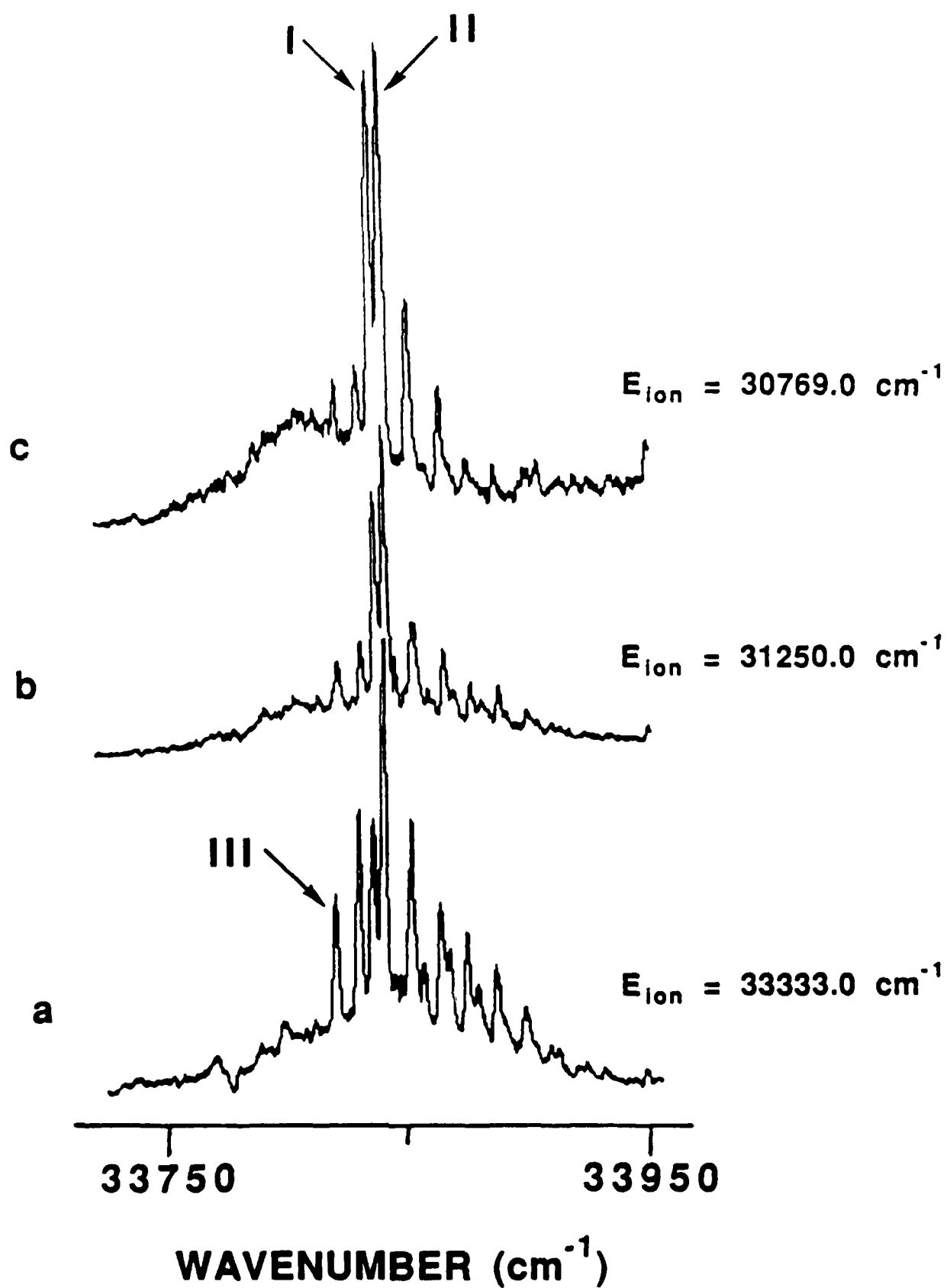
TOFMS of FLUORENE



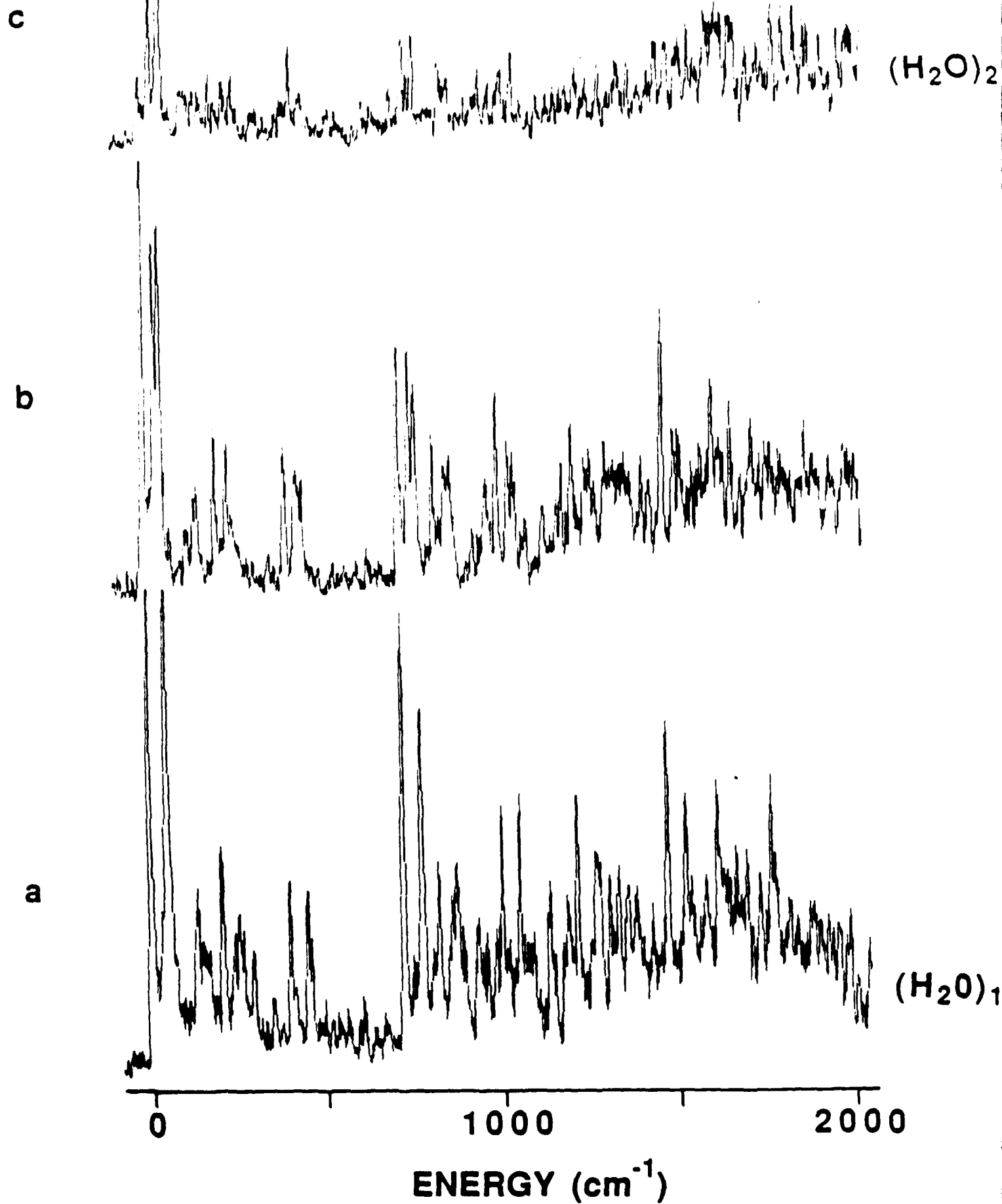
DE of FLUORENE



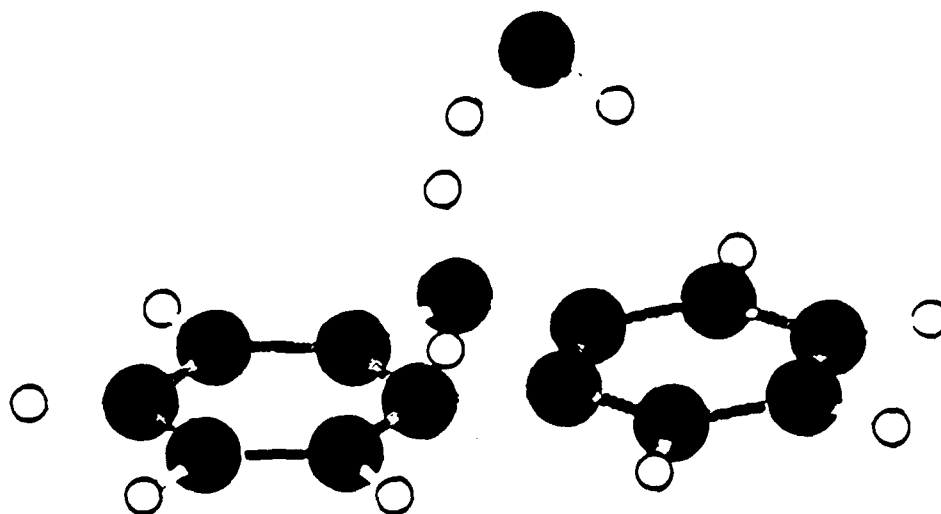
TOFMS of FLUORENE(H_2O)₁



DE of FLUORENE WATER CLUSTERS

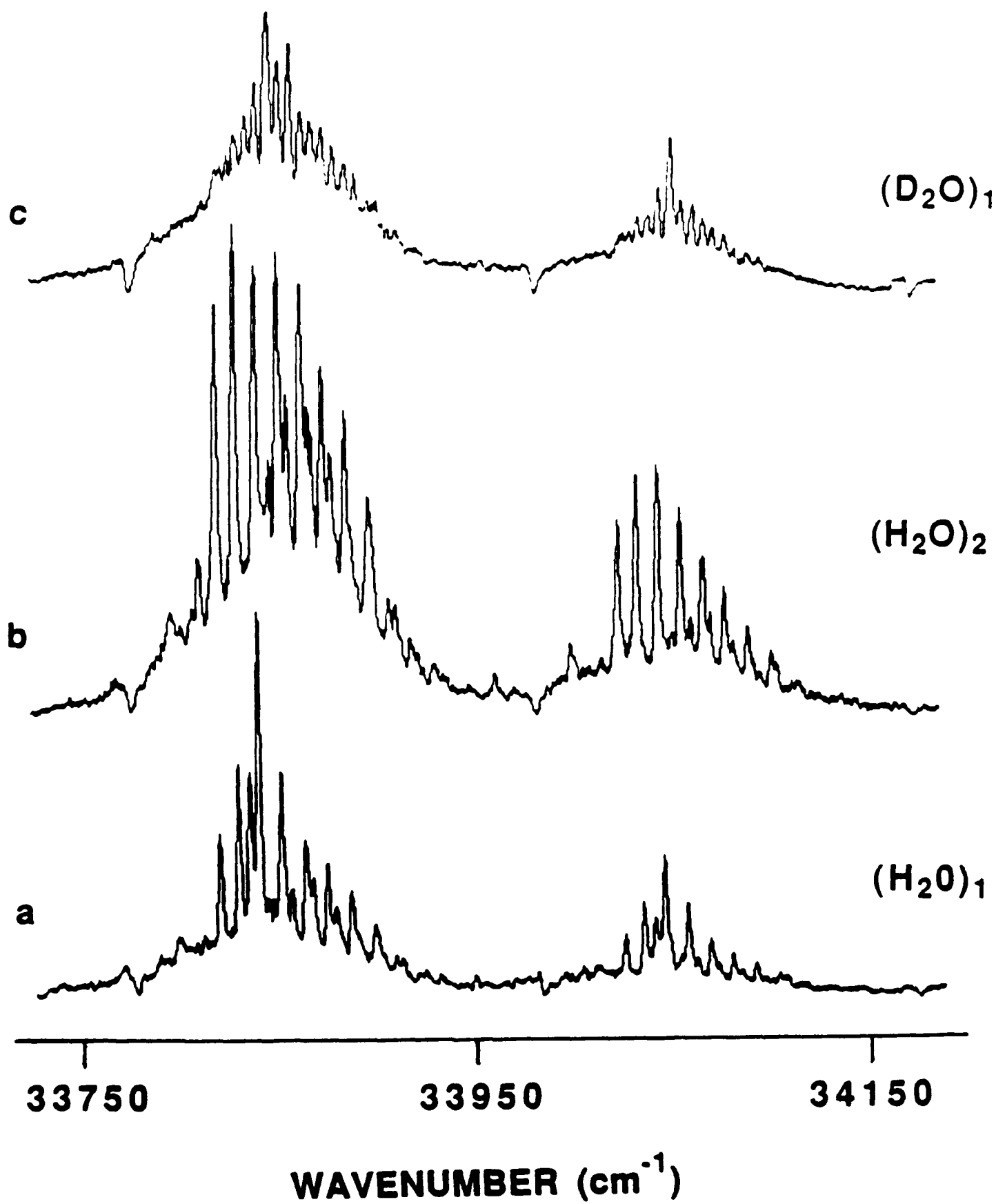


FLUORENE(H₂O)₁

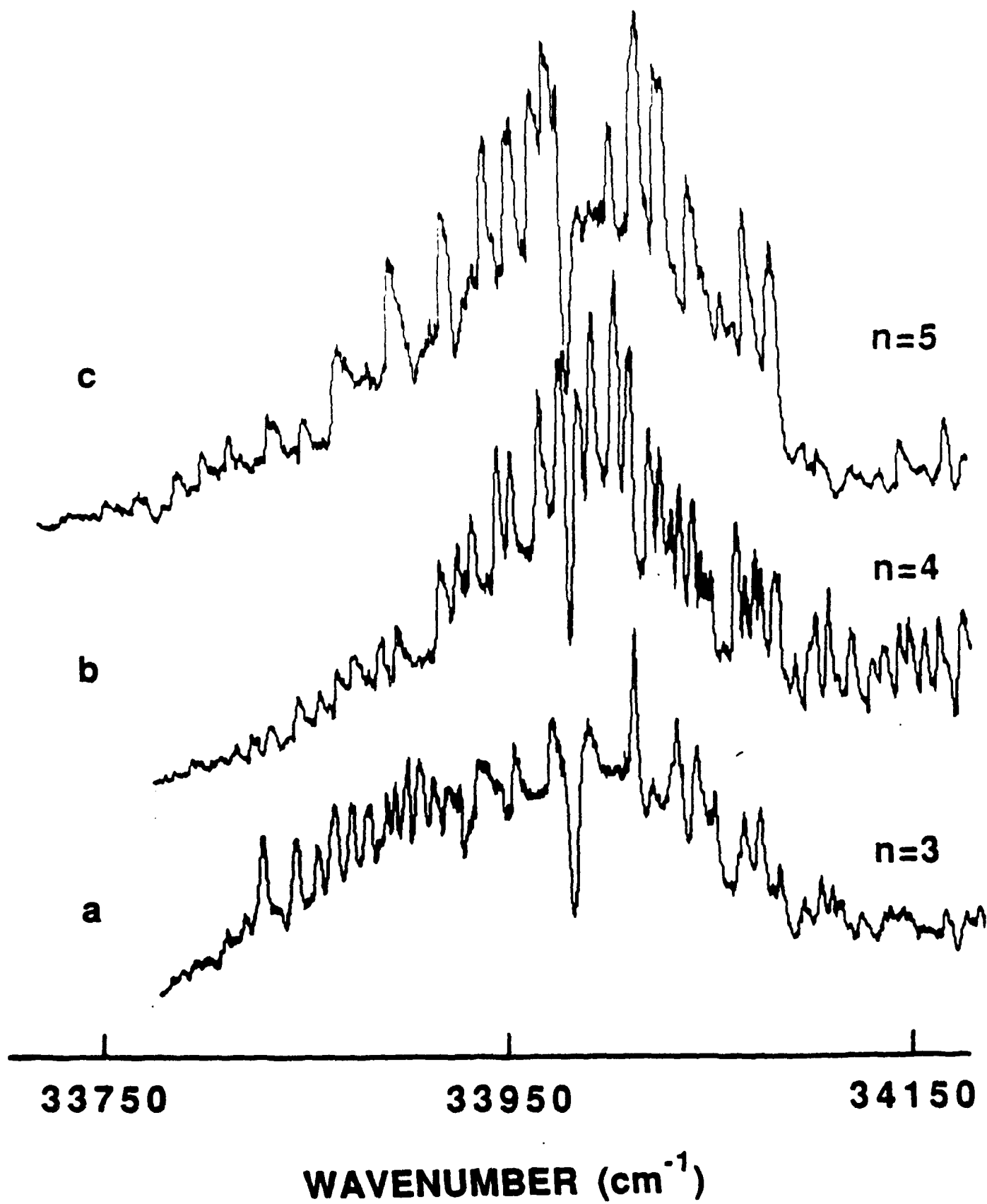


937 cm⁻¹

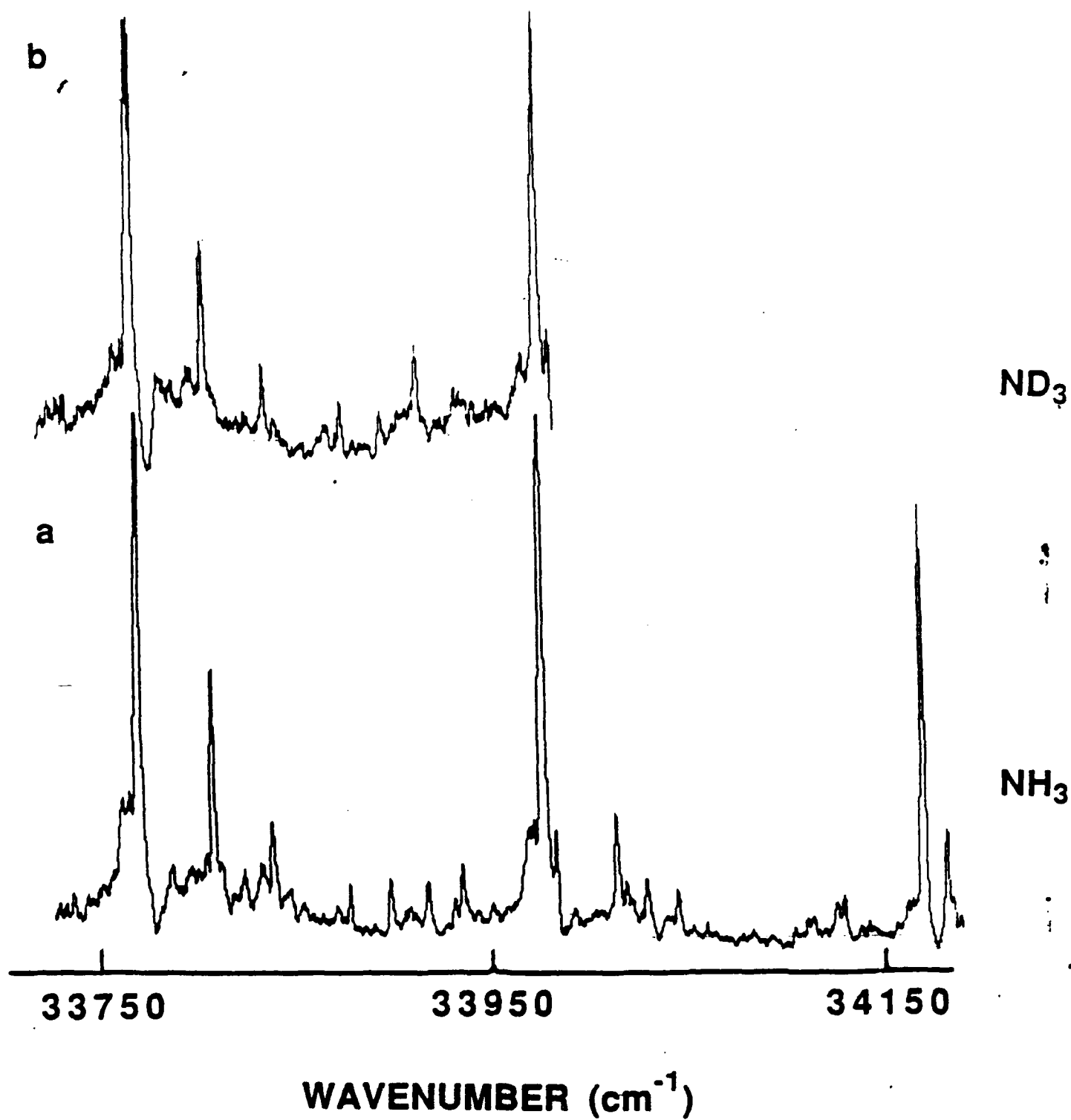
TOFMS of FLUORENE/WATER CLUSTERS



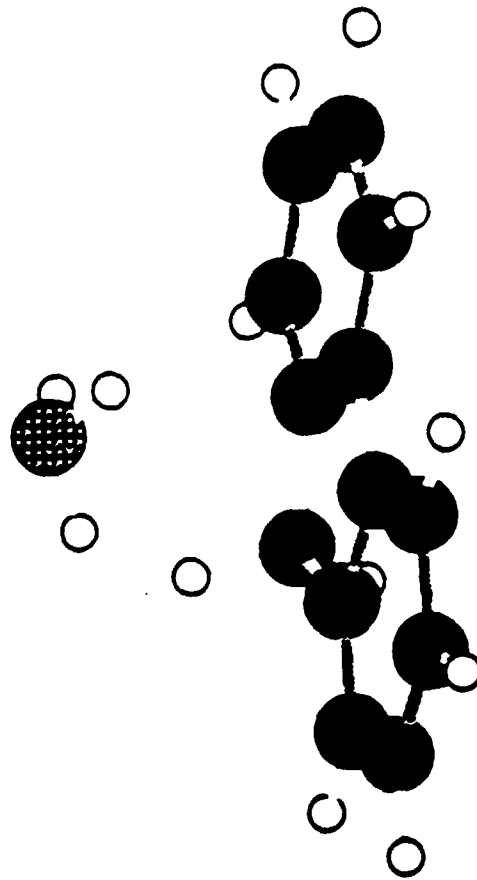
TOFMS of FLUORENE(H_2O) $_n$ CLUSTERS



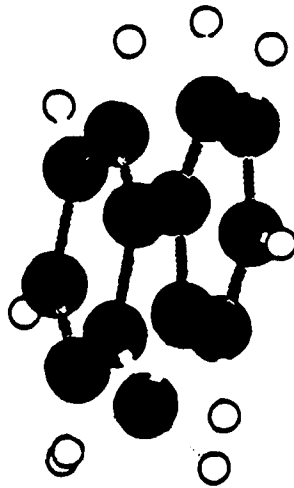
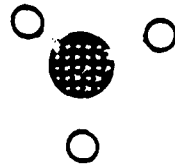
TOFMS of FLUORENE(AMMONIA)₁ CLUSTERS



FLUORENE(NH₃)₁

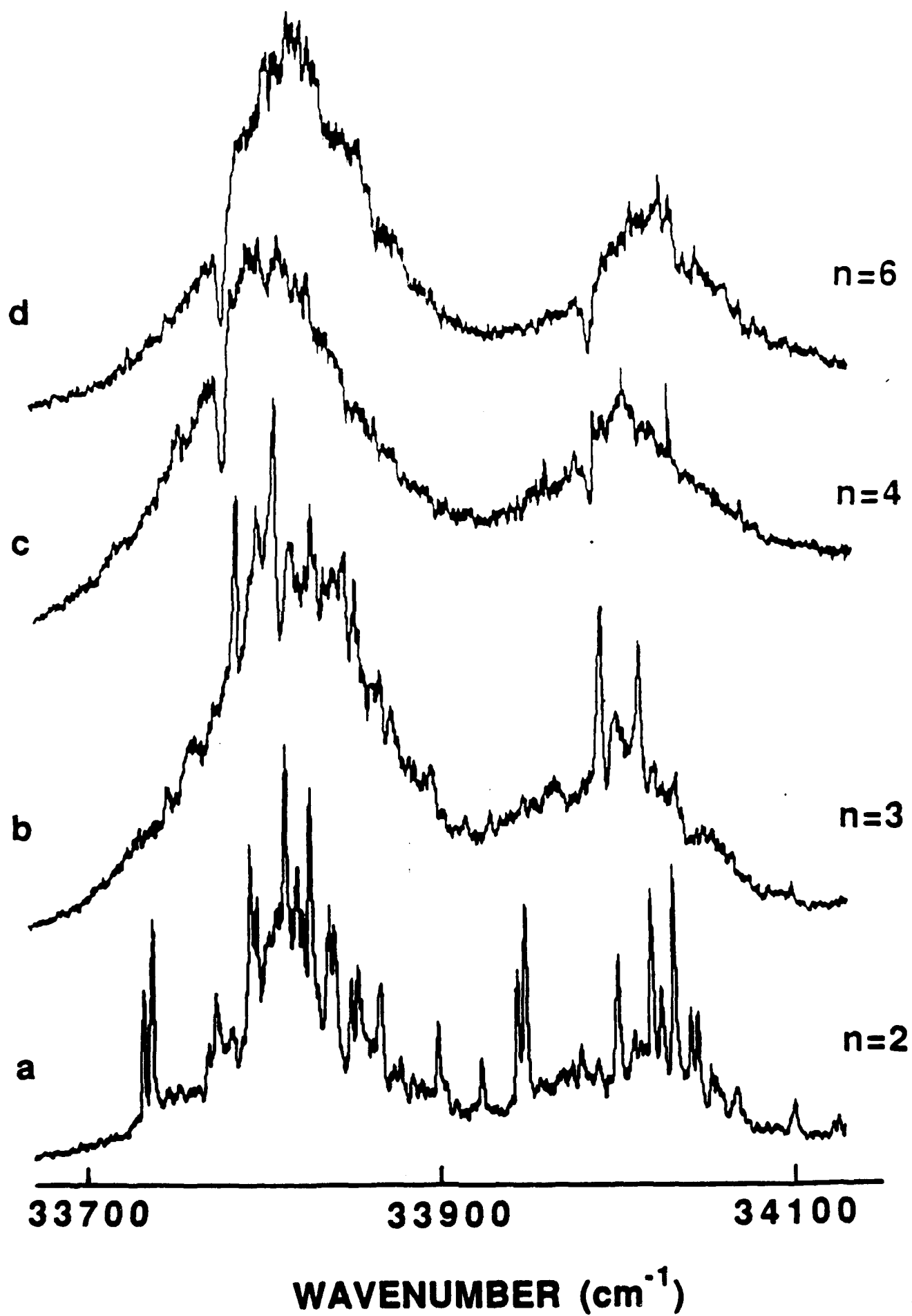


I 1063 cm⁻¹



II 447 cm⁻¹

TOFMS of FLUORENE(NH₃)_n CLUSTERS



DE of FLUORENE(NH₃)_n CLUSTERS

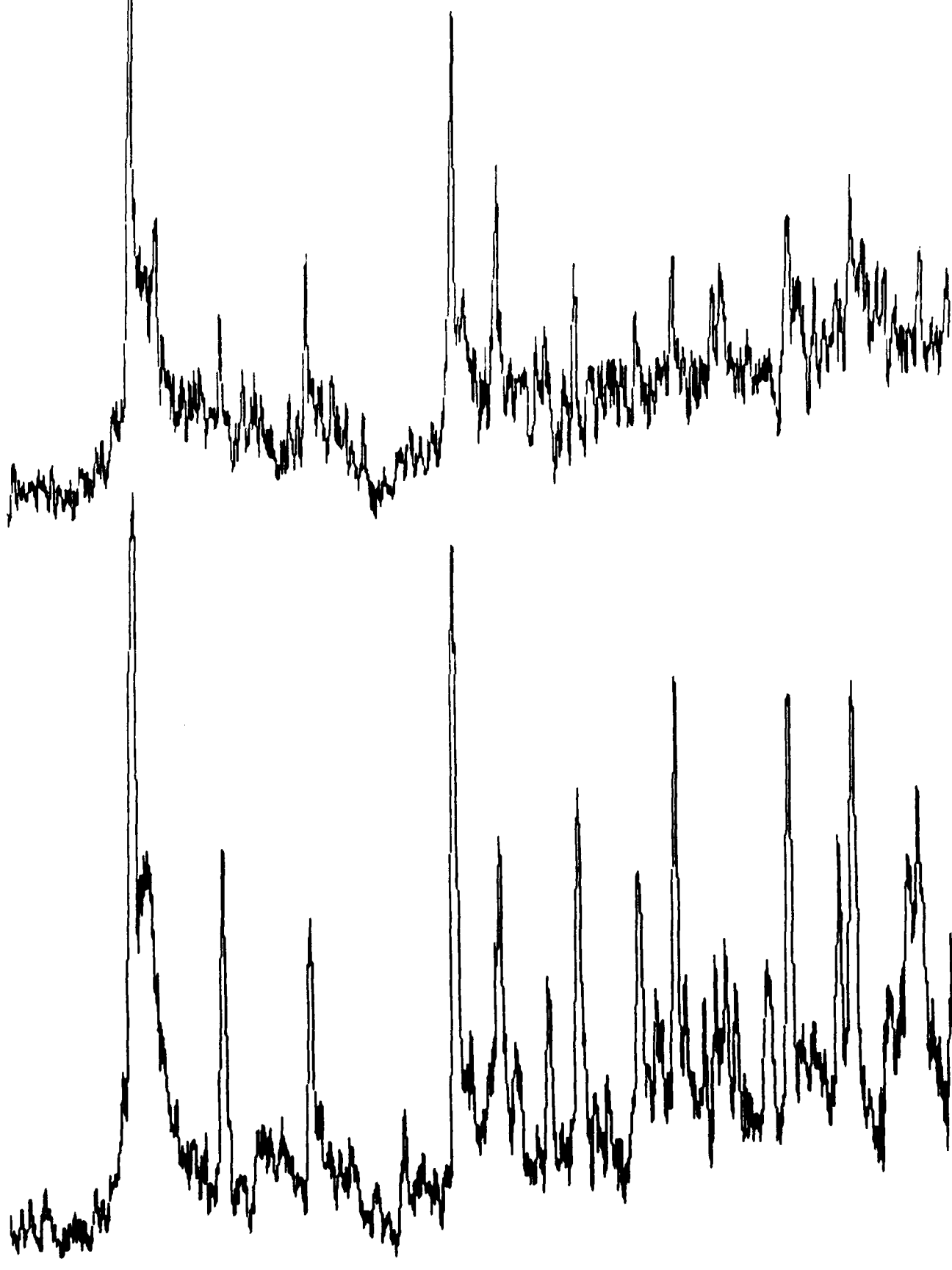
b

n=2

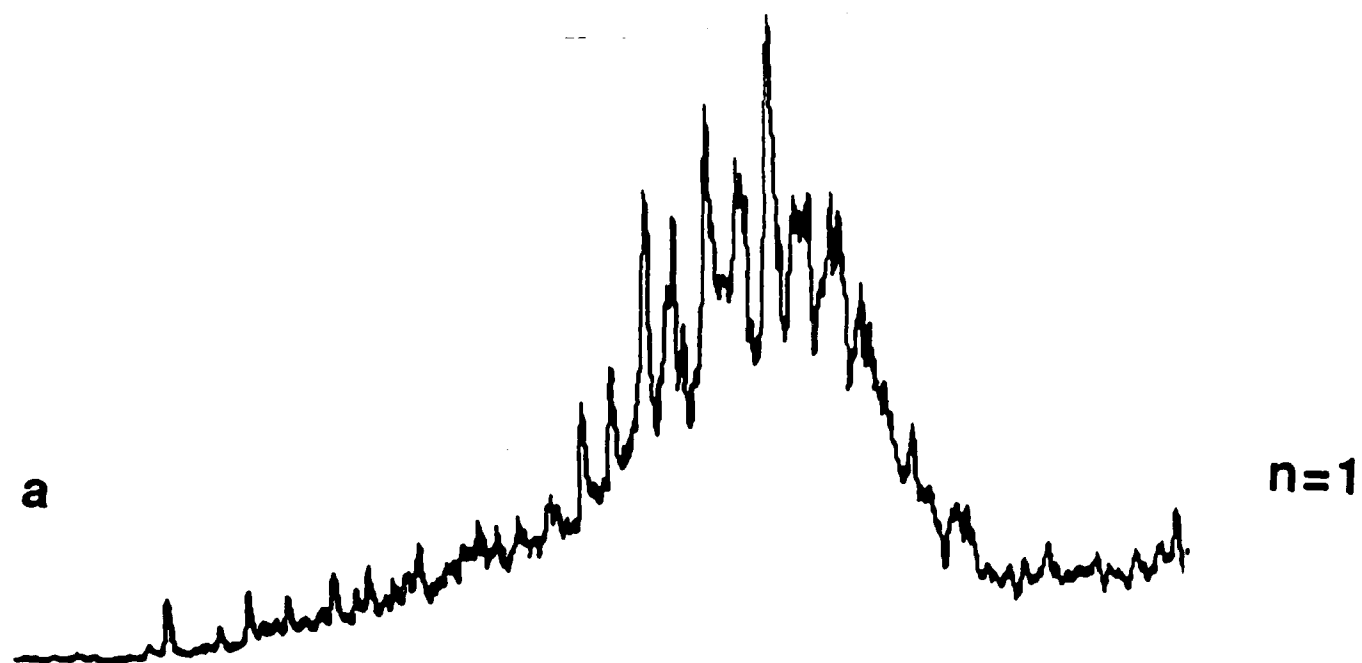
a

n=1

0 500 1000 1500
ENERGY (cm⁻¹)



TOFMS of FLUORENE(PIPERIDINE)_n CLUSTER



33650

33850

34050

WAVENUMBER (cm⁻¹)

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